The Effect of Iron Content on the Thermodynamic Properties of Syndiotactic Polypropylene/Iron Composites

Naveed Ahmad
Department of Chemical and Materials Engineering, College of Engineering, Northern Border University (NBU), Saudi Arabia
naveed.ahmad@nbu.edu.sa (corresponding author)

Farooq Ahmad
Department of Chemical and Materials Engineering, College of Engineering, Northern Border University (NBU), Saudi Arabia
faroog.amin@nbu.edu.sa

Received: 28 July 2023 | Revised: 3 September 2023 | Accepted: 5 September 2023

DOI: https://doi.org/10.48084/etasr.6241

ABSTRACT

This study investigated the influence of iron concentration on the thermodynamic properties of syndiotactic polypropylene (sPP)/iron composites in the melt phase in a series of samples with varying iron content, ranging from 0 to 10% with a step of 2%. The HYSYS software was used to estimate molecular weight, critical temperature (T_c), critical volume (V_c), and eccentricity (E_c). The results showed that all these properties changed as the iron content varied. The findings of this study confirmed that iron concentration has an impact on the mechanical and chain dynamic (microscopic) properties of polymer composites.

Keywords-polymer composites; thermodynamic properties; HYSYS; critical temperature; critical pressure; molecular weight; eccentricity

I. INTRODUCTION

Polymer composites have been known to have superior mechanical, thermal, and physical properties compared to polymers [1-6]. These characteristics change as the reinforcement phase changes [7-13]. Since polymer composites do not follow the same corrosion mechanisms as iron and steel, they are quickly replacing these materials. Due to these characteristics, polymer composites are versatile in many industrial applications, and their study has attracted much attention over the past few decades [3]. Fillers, such as iron content, clay, etc., alter not only the macrostructure properties of polymer composites but also their properties at the molecular level (microstructure properties) [17-20]. The thermal properties of polymer composites vary with the dose of the reinforcing phase [19].

Several studies have investigated syndiotactic polypropylene (sPP) composites. In [14], the rheological characteristics of sPP were studied, examining how the syndiotacticity of polypropylene affected the rheological characteristics, including the plateau modulus and entanglement molecular weight. When the syndiotacticity of sPP increased, a rise in the plateau modulus was observed. However, many polymers and polymer composite systems have not yet undergone such investigation. In [15], the rheological, thermodynamic, and multilayered film properties were studied on polyethylene oxide and montmorillonite clay, showing that an increase in the clay concentration caused a progressive increase in the storage and loss moduli. The thermal properties of composites and films were investigated using DSC and TGA, relating them to their microstructural characteristics, but without examining the relationship between molecular weight and other thermodynamic parameters, such as critical temperature, critical volume, and molecular weight.

In [16], it was examined how clay levels affect rheological variables, such as plateau modulus and entanglement molecular weight. Chinese bentonite clay was used to create clay and polypropylene composites, showing that increasing the clay concentration increased the plateau modulus and, as a result, lowered the entanglement molecular weight. In [18], the impact of thermodynamic variables on wood/plastic composites was studied. Plastics were melted at 180°C to prepare the composites, which were then dispensed onto wooden surfaces. When correlating the contact angle with the wood content, it was discovered that the contact angle decreased. At the polymer/wood interface, it was discovered that sanding results in decreased surface free energy and higher interfacial shear strengths. At higher temperatures, composite wetting was caused by polymer characteristics rather than interfacial tension at the polymer/wood contact. In [19], the thermal properties of sPP/iron composites were investigated by examining how the iron content affected thermal characteristics such as melting point, crystallization temperature, and glass transition temperature. The results showed that an increase in iron content affected thermal properties, such as melting point, crystallization, and glass transition temperatures, but this study did not assess how iron content affects thermodynamic properties, such as critical temperatures, critical volumes, molecular weights, and eccentricities.

Several studies have investigated the synthesis, thermal, and rheological investigation of polymers and composites made of polymers and iron. However, there is a lack of studies on the thermodynamic properties of sPP/iron composites or even estimation using software. As a result, this study investigated the relationship between the iron content and the thermodynamic characteristics of sPP/iron composites. Furthermore, this study estimated the thermodynamic properties of sPP/iron composites using HYSYS software, expanding previous studies [16, 19].

II. METHODOLOGY

Thermodynamic properties such as critical temperature (T_c), critical volume (V_c), molecular weight, and eccentricity (E_c) were calculated for sPP/iron composites with varying iron loadings ranging from 0 to 10% with a step size of 2%. The library components of the HYSYS software do not contain pure polymers and polymer/iron composites, but the simulation foundation manager allows for the creation of hypothetical components. If HYSYS is given two of the three base properties (molecular weight, normal boiling point, and density), it can estimate the critical temperature, critical volume, and eccentricity. To estimate the undetermined attributes, an estimation approach was used before installing the hypothetical components. This study used the default approach [21]. Les-Kesler, Bergman, and Cavett are three approaches that are accessible for the estimation of the critical temperature and other thermodynamic parameters. When choosing the default method, HYSYS selects according to the supplied data [22]. HYSYS chose the Pitzer approach to determine critical volume and eccentricity [23].

III. RESULTS AND DISCUSSION

This section presents results and a discussion of the effect of iron content on the thermodynamic properties of sPP/iron composites, examining critical temperature, critical pressure, critical volume, eccentricity, and molecular weight as a function of iron content, and finding that it greatly affects the thermodynamic properties of polymer composites.

A. Effect of Iron Content on Critical Temperature

The results showed that iron content is positively correlated with critical temperature. To reach the critical point, more energy is needed as the critical temperature rises, showing that composites made of sPP and iron have greater thermal strength. Figure 1 shows the connection between iron content and critical temperatures, pointing out that an increase in iron content improves thermal stability, and increases the intermolecular forces and the mechanical strength of sPP/iron composites. Previous studies [16, 19] confirm these two conclusions. The link between plateau modulus and clay concentrations was investigated in [16]. The plateau modulus, also known as the elastic modulus, demonstrates how the sPP/clay composites react mechanically. Composites made of sPP and clay with larger clay concentrations have higher plateau moduli and critical temperatures, showing that adding clay and iron to the filler increases thermal and mechanical strength. When the critical temperatures and melting points of the sPP/iron composites are matched, thermal stability is confirmed. Figure 2 illustrates the connection between the critical temperature and melting point temperatures, showing the increased critical and melting temperatures of sPP/iron composites with more iron content.

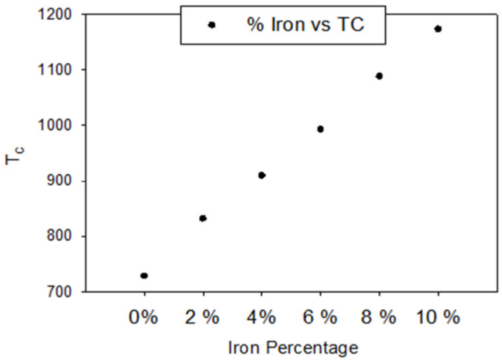

Fig. 1. Relationship between critical temperature and iron content of sPP/iron composites.

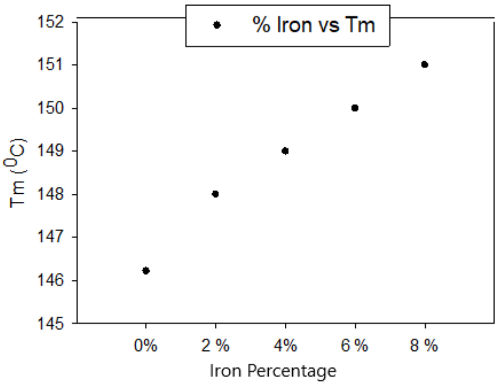

Fig. 2. Relationship between melting point temperature and iron content of sPP/iron composites.

B. Effect of Iron Content on Molecular Weight

According to Figure 3, there is a correlation between simulated molecular weight (Mw) values and the amount of iron in sPP/iron composites. The graph shows how the molecular weight of the sPP/iron composites increases as the iron content increases. The molecular weight of polymer and polymer composites influences how quickly they relax [24]. These results can be further confirmed by [17], by matching the cross-over frequency of the master curves (relaxation time) and simulated molecular weights of the polymer composites.

Polymer composites of higher filler content have higher relaxation time and molecular weights.

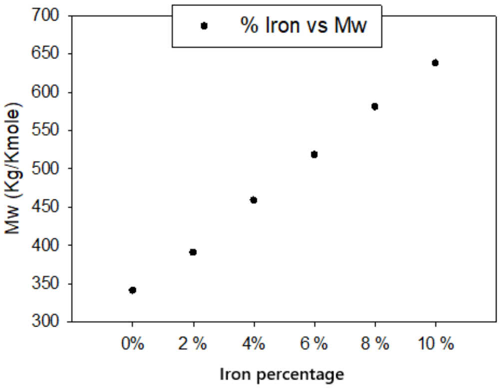

Fig. 3. Relationship between molecular weight and iron content of sPP/iron composites.

C. Effect of Iron Content on Critical Volume

Critical volume is based on the volume of the material observed [25]. The critical volume was estimated for each sPP/iron sample. Figure 4 shows the connection between critical volume and iron concentrations, pointing out that an increase in iron concentration increases critical volume, which is consistent with [25].

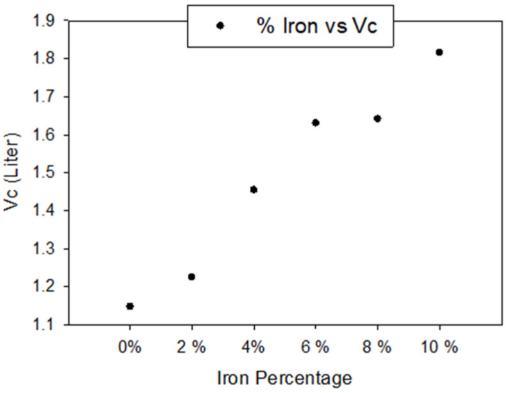

Fig. 4. Relationship between critical volume and iron content of sPP/iron composites.

D. Effect of Iron Contents on Eccentricity

Eccentricity is a metric for the way the crystals or monomers of a material are organized [26]. The eccentricity of all sPP/iron composites was simulated. Figure 5 shows the correlation between eccentricity and iron concentrations, demonstrating that eccentricity increased with increasing iron content. This might have something to do with how iron content affects crystallinity and, therefore, the eccentricity of sPP/iron composites. This finding can be further verified from the melting points of sPP/iron composites. Polymer composites with a higher iron content have higher melting points, indicating that the monomers are organized more consistently and hence require more energy to melt.

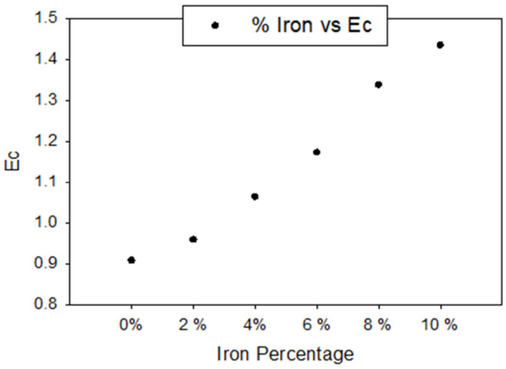

Fig. 5. Relationship between eccentricity and iron content of sPP/iron composites.

These results show how the iron content affects the thermodynamic properties of sPP/iron composites. An increase in iron content increased the critical temperature and altered other thermodynamic parameters. This is because an increase in iron content increases the strength and thermal stability of sPP/iron composites, as more energy is required to reach the critical temperature. Figure 2 shows the relationship between the melting point and the iron content, demonstrating that the melting point of sPP/iron composites increases with increasing iron content. This indicates that the iron content affects the intermolecular forces of the sPP/iron composites. It can be concluded that iron content affects the molecular architecture of sPP/iron composites, and hence their thermal and microstructure properties.

IV. CONCLUSION

Thermodynamic analysis provides wide information about the properties of materials, as it provides information both at the macromolecular and molecular levels. This study demonstrates that the iron content affects not only the other properties but also the thermodynamic properties of sPP/iron composites. Thermodynamic properties were determined using the HYSYS software, and these properties were analyzed as functions of the iron content. The critical temperature, critical volume, molecular weight, and eccentricity were found to increase with increasing iron content, reflecting the fact that iron content affects the polymer chain at both macromolecular and molecular levels. The results of this study reveal that thermodynamic information can be used to predict both the molecular and macromolecular properties of any polymer or polymer composite.

ACKNOWLEDGMENT

The authors wish to acknowledge the approval and support of this research study by grant no. ENGA-2022-11-1819 from the Deanship of Scientific Research at Northern Border University, Kingdom of Saudi Arabia.

REFERENCES

[1] D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, and T. T. Wenzel, "Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization," *Science*, vol. 312, no. 5774, pp. 714–719, May 2006, https://doi.org/10.1126/science.1125268.

[2] V. C. Gibson, "Shuttling Polyolefins to a New Materials Dimension," *Science*, vol. 312, no. 5774, pp. 703–704, May 2006, https://doi.org/10.1126/science.1127258.

[3] A. Ghanbari, M. C. Heuzey, P. J. Carreau, and M. T. Ton-That, "Morphological and rheological properties of PET/clay nanocomposites," *Rheologica Acta*, vol. 52, no. 1, pp. 59–74, Jan. 2013, https://doi.org/10.1007/s00397-012-0667-1.

[4] G. K. Jatav, R. Mukhopadhyay, and N. De, "Characterization of Swelling Behavior of Nanoclay Composite," *International Journal of Innovative Research in Science, Engineering and Technology*, vol. 2, no. 5, pp. 1560–1563, May 2013.

[5] M. Doi, S. F. Edwards, and S. F. Edwards, *The Theory of Polymer Dynamics*. Oxford, UK: Clarendon Press, 1988.

[6] L. J. Fetters, D. J. Lohse, D. Richter, T. A. Witten, and A. Zirkel, "Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties," *Macromolecules*, vol. 27, no. 17, pp. 4639–4647, Aug. 1994, https://doi.org/10.1021/ma00095a001.

[7] A. Eckstein *et al.*, "Determination of Plateau Moduli and Entanglement Molecular Weights of Isotactic, Syndiotactic, and Atactic Polypropylenes Synthesized with Metallocene Catalysts," *Macromolecules*, vol. 31, no. 4, pp. 1335–1340, Feb. 1998, https://doi.org/10.1021/ma971270d.

[8] J. M. Carella, W. W. Graessley, and L. J. Fetters, "Effects of chain microstructure on the viscoelastic properties of linear polymer melts: polybutadienes and hydrogenated polybutadienes," *Macromolecules*, vol. 17, no. 12, pp. 2775–2786, Dec. 1984, https://doi.org/10.1021/ma00142a059.

[9] S. Bagheri-Kazemabad *et al.*, "Morphology, rheology and mechanical properties of polypropylene/ethylene–octene copolymer/clay nanocomposites: Effects of the compatibilizer," *Composites Science and Technology*, vol. 72, no. 14, pp. 1697–1704, Sep. 2012, https://doi.org/10.1016/j.compscitech.2012.06.007.

[10] M. Sarkar, K. Dana, S. Ghatak, and A. Banerjee, "Polypropylene-clay composite prepared from Indian bentonite," *Bulletin of Materials Science*, vol. 31, no. 1, pp. 23–28, Feb. 2008, https://doi.org/10.1007/s12034-008-0005-5.

[11] Y. Xiang, Z. Peng, and D. Chen, "A new polymer/clay nano-composite hydrogel with improved response rate and tensile mechanical properties," *European Polymer Journal*, vol. 42, no. 9, pp. 2125–2132, Sep. 2006, https://doi.org/10.1016/j.eurpolymj.2006.04.003.

[12] C. Liu, J. He, E. van Ruymbeke, R. Keunings, and C. Bailly, "Evaluation of different methods for the determination of the plateau modulus and the entanglement molecular weight," *Polymer*, vol. 47, no. 13, pp. 4461–4479, Jun. 2006, https://doi.org/10.1016/j.polymer.2006.04.054.

[13] J. D. Ferry, *Viscoelastic Properties of Polymers*. New York, NY, USA: John Wiley & Sons, 1980.

[14] N. Ahmad, R. Di Girolamo, F. Auriemma, C. De Rosa, and N. Grizzuti, "Relations between Stereoregularity and Melt Viscoelasticity of Syndiotactic Polypropylene," *Macromolecules*, vol. 46, no. 19, pp. 7940–7946, Oct. 2013, https://doi.org/10.1021/ma401469a.

[15] S. Y. Gu, J. Ren, and Q. F. Wang, "Rheology of poly(propylene)/clay nanocomposites," *Journal of Applied Polymer Science*, vol. 91, no. 4, pp. 2427–2434, 2004, https://doi.org/10.1002/app.13403.

[16] N. Ahmad and E. Fouad, "Influence of Clay Contents on Rheology of Syndiotactic Polypropylene/Clay Composites," *Arabian Journal for Science and Engineering*, vol. 42, no. 4, pp. 1537–1543, Apr. 2017, https://doi.org/10.1007/s13369-016-2389-7.

[17] N. Ahmad, E. Fouad, and F. Ahmad, "Effect of Shear Flow on Crystallization of Sydiotactic Polypropylene/Clay Composites," *Engineering, Technology & Applied Science Research*, vol. 8, no. 4, pp. 3108–3112, Aug. 2018, https://doi.org/10.48084/etasr.2079.

[18] P. Rezaee Niaraki and A. Krause, "Correlation between physical bonding and mechanical properties of wood–plastic composites: part 2: effect of thermodynamic factors on interfacial bonding at wood–polymer interface," *Journal of Adhesion Science and Technology*, vol. 34, no. 7, pp. 756–768, Apr. 2020, https://doi.org/10.1080/01694243.2019.1689628.

[19] A. Z. Al-Khazaal and N. Ahmad, "A Study of the Impact of Iron Content on the Thermal Response of the sPP/Fe Composites," *Engineering, Technology & Applied Science Research*, vol. 12, no. 3, pp. 8555–8558, Jun. 2022, https://doi.org/10.48084/etasr.4884.

[20] N. Ahmad, F. Ahmad, and I. Alenezi, "Influence of Starch Content on the Thermal and Viscoelastic Properties of Syndiotactic Polypropylene/Starch Composites," *Engineering, Technology & Applied Science Research*, vol. 11, no. 3, pp. 7228–7232, Jun. 2021, https://doi.org/10.48084/etasr.4161.

[21] D. C. Cruz-Forero, O. A. González-Ruiz, and L. J. López-Giraldo, "Calculation of thermophysical properties of oils and triacylglycerols using an extended constituent fragments approach," *CT&F-Ciencia, Tecnología y Futuro*, vol. 5, no. 1, pp. 67–82, 2012.

[22] C. Li, W. Jia, and X. Wu, "Application of Lee-Kesler equation of state to calculating compressibility factors of high pressure condensate gas," *Energy Procedia*, vol. 14, pp. 115–120, Jan. 2012, https://doi.org/10.1016/j.egypro.2011.12.904.

[23] Z. Bakher and M. Kaddami, "Thermodynamic properties and Pitzer parameter determination for orthophosphoric acid from freezing point and isopiestic measurement data," *Brazilian Journal of Chemical Engineering*, vol. 35, pp. 1153–1162, 2018.

[24] W. Thimm, C. Friedrich, M. Marth, and J. Honerkamp, "An analytical relation between relaxation time spectrum and molecular weight distribution," *Journal of Rheology*, vol. 43, no. 6, pp. 1663–1672, 1999.

[25] B. J. Taylor and M. B. Maple, "Formula for the critical temperature of superconductors based on the electronic density of states and the effective mass," *Physical review letters*, vol. 102, no. 13, 2009, Art. no. 137003.

[26] M. F. M. Fahmy and O. A. Farghal, "Eccentricity-based design-oriented model of fiber-reinforced polymer-confined concrete for evaluation of load-carrying capacity of reinforced concrete rectangular columns," *Journal of Reinforced Plastics and Composites*, vol. 35, no. 23, pp. 1734–1758, Dec. 2016, https://doi.org/10.1177/0731684416667239.